

The maximum entropy production principle and linear irreversible processes

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(Dated: March 22, 2010)

Abstract

It is shown that Onsager's principle of the least dissipation of energy is equivalent to the maximum entropy production principle. It is known that solutions of the linearized Boltzmann equation make extrema of entropy production. It is argued, in the case of stationary processes, that this extremum is a maximum rather than a minimum.

PACS numbers: 65.40.gd

Keywords: entropy production; linear nonequilibrium thermodynamics, linearized Boltzmann equation

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I. INTRODUCTION

It was Ehrenfest (Enzykl. Math. Wissensch, IV, 2(II) fasc.6, p82, note23, 1912) who first asked whether a function exists which, like entropy in the equilibrium state of an isolated system, achieves its extreme value in a stationary non-equilibrium state.

There are various results and formulations of irreversible thermodynamics based on the extremum of entropy production. They are related either to the minimum or maximum entropy production. The well known example based on minimum entropy production is Prigogine theorem [1].

There are several different results that concern maximum entropy production (MEP). Ziegler applied the principle of maximum entropy production in thermomechanics [2]. It states that the rate of entropy production under prescribed forces should be maximum. Paltridge [3] has formulated empirically MEP principle in order to describe the Earth climate. Apart from details of his model (like albedo or cloudiness) the main features of his model are steady incoming sun radiation, outgoing radiation proportional to the fourth power of the local annual average temperature and horizontal heat flux from equator to poles. There are no boundary conditions on atmosphere. Paltridge has proposed that steady state is the state of maximum entropy production due to the latitudinal heat transport. His predictions of the annually average distribution of the temperature of atmosphere (and some other climatic parameters) fit very well measured values. Kohler [4] has started from the Boltzmann's transport equation and has shown that the solution for the velocity distribution function of rarefied gas, in stationary state close to the equilibrium, is the state of extremum entropy production. He has argued that extremum type depends on the choice of the constraint. We show in this paper that constraint that leads to the stationary state as the state of the minimum entropy production is not consistent with his starting assumption. We argue here that rarefied gas in the stationary state close to equilibrium is in the MEP state.

Recently Jaynes' principle of maximum information entropy (MaxEnt) has been exploited to derive the MEP principle. Dewar [5, 6] has introduced paths as possible trajectories of the system in phase space. Then using the MaxEnt procedure he has shown , under some assumptions, that the most probable development of the system is accompanied with MEP. Niven [7] has applied MaxEnt using the values of fluxes as variables and he found that the stationary state of the system is the MEP state.

At first sight minimum and maximum entropy production results seem to contradict each other. But if one considers starting assumptions one finds that these assumptions are different. Thus these results are independent of one another [8, 9]

In this paper we focus on Onsager's principle of least dissipation of energy and show that this principle is equivalent to MEP principle. Secondly, as we have already noted, we show that Kohler interpretation of stationary state of rarefied gas close to the equilibrium should be restricted only on the constraint that it is consistent with the interpretation of this state as the MEP state.

This is the first of three papers in a series and are referred to as papers I, II and III. In paper II we discuss whether stationary or relaxation processes are suitable for the formulation of principles. We argue in favour of relaxation processes. In paper III we apply MaxEnt formalism to relaxation processes and we derive the MEP principle as its corollary.

II. THE PRINCIPLE OF THE LEAST DISSIPATION OF ENERGY AND LINEAR NONEQUILIBRIUM THERMODYNAMICS

Onsager's famous papers [10, 11] examine linear nonequilibrium thermodynamics. The first sections of these papers examine reciprocal relations. The following sections are devoted to the formulation of linear nonequilibrium thermodynamics. Onsager has employed the principle of the least dissipation of energy. In the second part of his second paper [11], Onsager has applied the principle of the least dissipation energy to the general linear nonequilibrium process.

A linear relationship between n independent thermodynamic forces $\{X_i\}$ and their conjugated fluxes $\{j_i\}$,

$$X_i = \sum_j R_{ij} j_j, \quad (1)$$

exists for the system close to equilibrium. The density of the entropy production is equal to the product of the thermodynamic forces and conjugated fluxes [1], [12]. The total entropy production is

$$\sigma = \int \sum_{j=1}^n X_j j_j dV. \quad (2)$$

In his second famous paper Onsager [11] has introduced the dissipation function

$$\Phi = \frac{1}{2} \int \sum_{i,j=1}^n R_{ij} j_i j_j dV, \quad (3)$$

and formulated the principle of the least dissipation of energy,

$$\sigma - \Phi = \textit{maximum}. \quad (4)$$

The variational procedure

$$\delta [\sigma - \Phi] = 0, \quad (5)$$

gives the system of equations (1). In other words, the linear irreversible thermodynamics can be inferred from the principle of the least dissipation of energy.

III. THE MEP PRINCIPLE AND LINEAR NONEQUILIBRIUM THERMODYNAMICS

An alternative approach to linear nonequilibrium thermodynamics is based on the phenomenological fact that nonequilibrium processes are characterized by fluxes. Therefore, physical quantities relevant for a description of the time development of the system must be functions of fluxes. The standard approach to the nonequilibrium thermodynamics is based on the laws of conservation of mechanical physical quantities mass, momentum and energy. The next step is to add heat as the additional mechanism of the exchange of energy between systems. Then assuming local equilibrium one comes to the density of entropy production written as the sum of products of heat flux and thermal thermodynamic force and viscous pressure tensor and strain tensor divided by temperature. This result serves as the basis for the canonical form of the second postulate of irreversible thermodynamics that reads: Entropy production can be always written as the sum of products of thermodynamic forces and corresponding fluxes [12, 13]. Thermodynamic forces and fluxes are not independent quantities. In principle fluxes determine forces and vice versa. Having in mind this fact and the second postulate of irreversible thermodynamics we can say that the dynamical state of the system is described only by fluxes, or equivalently by thermodynamic forces.

Entropy production is a basic, characteristic quantity of a nonequilibrium state. If the system is close to the equilibrium state we can make the Taylor expansion of the density of

entropy production $d\sigma/dV$ in fluxes up to the second order,

$$\frac{d\sigma}{dV} = A + \sum_i B_i j_i + \sum_{i,j} R_{ij} j_i j_j. \quad (6)$$

Here j_i is the mean value of the i^{th} flux. The first term on the right-hand side of this equation vanishes since there is no entropy production in the equilibrium state. Coefficients B_i and R_{ij} are the property of the system in equilibrium state. Entropy production does not depend on the direction of the flux flow, that is to say, it must be invariant under the replacement of $\{j_i\} \rightarrow \{-j_i\}$. This means that coefficients that multiply the odd power of fluxes vanish, that is, $B_i = 0$. In the lowest order, entropy production is the bilinear function of fluxes,

$$\sigma = \sum_{i,j} \int_V R_{ij} j_i j_j d\mathbf{r} > 0. \quad (7)$$

Comparison of Eqs. (7) and (3) shows that the dissipation function is in fact entropy production written in the space of fluxes. When a system is close to equilibrium with locally well defined intensive thermodynamic quantities the entropy production is given by Eq. (2), [1], [12].

It is pointed in the introductory part of this Section that canonical form of entropy production (2) comes from the law of conservation of energy. Then equation,

$$\int_V \left(\sum_i X_i j_i - \sum_{i,j} R_{ij} j_i j_j \right) d\mathbf{r} = 0. \quad (8)$$

is the constraint imposed the entropy production due to the law of conservation of energy.

We seek the maximum entropy production (7) taking into account the constraint (8). The standard procedure [14] is to find the maximum of the functional

$$F = \sum_{i,j} \int_V R_{ij} j_i j_j d\mathbf{r} + \lambda \int_V \left[\sum_i X_i j_i - \sum_{i,j} R_{ij} j_i j_j \right] d\mathbf{r}. \quad (9)$$

A standard variational calculus of extremum values combined with the constraint (8) gives $\lambda = 2$ and F_l becomes

$$F = - \sum_{i,j} \int_V R_{ij} j_i j_j d\mathbf{r} + 2 \int_V \sum_i X_i j_i d\mathbf{r}.$$

This is an equation of a quadratic surface turned upside down. The corresponding extremum of F is maximum. The system of equations that determines the point of maximum, $\partial F / \partial j_i = 0$, is just a system of linearly coupled thermodynamic forces and fluxes (1).

From Eq. (7) follows $R_{ij} = R_{ji}$ i.e. Onsager's reciprocal relations. In short, linear nonequilibrium thermodynamics and Onsager's reciprocity relations follow from the MEP principle.

A problem analogous to this is the problem of biochemical cycle kinetics close to the equilibrium state. Starting from the assumption that the energy conservation law is valid for a whole network of biochemical reactions we have showed that fluxes are distributed in such a way to produce maximum entropy [15].

In references [16, 17] we have considered a linear planar electric network held at a constant temperature. There is only a temperature gradient between network and surroundings. Physically this can be achieved using thermally high and poor conducting material for a network and surroundings, respectively. There is no coupling between electric and heat currents. Only electric currents are coupled via electromotive forces. Assuming that the stationary state is the state of maximum possible generated heat the Kirchhoff loop law is derived [16, 17]. The principle of the maximum heat dissipation is closely related to the MEP principles.

Using mesh currents the law of charge conservation has been taken implicitly. The energy conservation law is used explicitly as the constraint. If one only takes charge conservation law one comes to the conclusion that stationary state is state of minimum generated heat [18]. We shall dwell more on this question in the paper II submitted to this special issue.

We note that two of us (P.Ž. and D.J.) have considered the heat flow in the anisotropic crystal. It is shown in this special example that the principle of the least dissipation of energy applied by Onsager in reference [10] is equivalent to the MEP principle [19].

IV. THE LINEARIZED BOLTZMANN EQUATION AND THE EXTREMUM OF ENTROPY PRODUCTION

The important influence of constraints at extrema of entropy production can be seen in the case of linearized Boltzmann equation.

Here we follow the elegant approach given in reference [9]. The Boltzmann equation is valid for rarefied gas where collisions are very well defined events. One seeks the one-particle

distribution function $f(\mathbf{r}, \mathbf{v}, t)$ satisfying the equation,

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \mathbf{v} \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \frac{\partial f}{\partial \mathbf{v}} = I. \quad (10)$$

Here the two terms on the left-hand side of equation describe the change in the number of molecules in a given element of the phase space due to the collisionless motion of the molecule in the outer field \mathbf{F} . The right-hand side of the equation describes the net change in the number of molecules in a given element of the velocity space due to molecule collisions. Assuming the instantaneous change of molecule velocities in the collisions and taking into account the conservation laws in collisions the integral can be written in the form [20]

$$I = \int \int (\tilde{f}\tilde{f}' - ff')q d\sigma(q, \mathbf{e}) d\mathbf{v}'. \quad (11)$$

Here $f = f(\mathbf{r}, \mathbf{v}, t)$; $f' = f(\mathbf{r}, \mathbf{v}', t)$ and $\tilde{f} = f(\mathbf{r}, \tilde{\mathbf{v}}, t)$; $\tilde{f}' = f(\mathbf{r}, \tilde{\mathbf{v}}', t)$ are the distribution functions of particles before and after collision, respectively. In addition, $q = v' - v$ is the magnitude of relative velocity of particles before collisions, $\mathbf{e} = (\tilde{\mathbf{v}} - \mathbf{v})/|\tilde{v} - v|$ is a unit vector parallel to the velocity change of one particle in collision and $d\sigma(q, \mathbf{e})$ is the differential cross section. It is known from collision theory that differential cross section depends on interaction potential, relative velocity q and unit vector \mathbf{e} , i.e. on the scattering angle [20].

In the case of local equilibrium, intensive variables (temperature, concentration) are well defined functions of the space. Then one assumes the approximate solution of Eq. (10) [4], [9].

$$f = f_0(1 + \Psi(\mathbf{v})), \quad (12)$$

where

$$f_0 = n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mV^2}{2kT}\right) \quad (13)$$

is the Maxwell-Boltzmann distribution.

Due to the assumption of local equilibrium the perturbed function must not contribute to the prescribed intensive parameters like temperature, mean velocity and density. Then

$$\int f_0 \Psi(\mathbf{v}) d\mathbf{v} = 0, \quad \int f_0 \Psi(\mathbf{v}) V d\mathbf{v} = 0, \quad \int f_0 \Psi(\mathbf{v}) \frac{mV^2}{2} d\mathbf{v} = 0. \quad (14)$$

Now the collision integral up to the first order of the perturbed term becomes

$$I(f) = \int \int \int f_0 f'_0 (\tilde{\Psi} + \tilde{\Psi}' - \Psi - \Psi') q d\sigma(q, \mathbf{e}) d\mathbf{v}' = \hat{O}\Psi. \quad (15)$$

The designation of Ψ functions is the same as the distribution functions in Eq. (11).

Operator \hat{O} [4], [9] is linear and has the following properties

$$\hat{O}(\alpha A + \beta B) = \alpha \hat{O}A + \beta \hat{O}B, \quad (16)$$

$$\int A \hat{O}B d\mathbf{v} = \int B \hat{O}A d\mathbf{v}, \quad (17)$$

$$\int A \hat{O}A d\mathbf{v} \geq 0. \quad (18)$$

If we designate the left-hand side of Boltzmann equation (10) with $-Z$ it becomes

$$Z = -\hat{O}\Psi. \quad (19)$$

Multiplying the linearized Boltzmann equation with $-k \ln f$ and integrating over velocity space we get

$$\frac{\partial s}{\partial t} + \nabla \cdot \mathbf{j}_s = k \int \Psi \hat{O}\Psi d\mathbf{v}. \quad (20)$$

Here $s = -k \int f \ln f d\mathbf{v}$ is the density of entropy and $\mathbf{j}_s = -k \int \mathbf{v} f \ln f d\mathbf{v}$ is the flux of entropy. Entropy looks like a fluid. The left-hand side of Eq. (20) is the total time change of the density of entropy, i.e. it is the density of the entropy production. Then, according to the aforementioned equation collisions between molecules described by function Ψ are the sources of entropy production. There are a lot of functions obeying conditions (14). We choose those distribution functions that obey the additional condition

$$\int Y Z d\mathbf{v} = - \int Y \hat{O}Y d\mathbf{v}. \quad (21)$$

Function Y is not the solution of the Boltzmann equation, i.e.

$$Z \neq -\hat{O}Y. \quad (22)$$

Y can be interpreted as a trial distribution function. The corresponding entropy production due to this distribution is

$$\frac{\partial s_Y}{\partial t} + \nabla \cdot (\mathbf{j}_s)_Y = k[Y, \hat{O}Y]. \quad (23)$$

If the temperature gradient in x direction is the only thermodynamic force, the left-hand side of the equation (21) can be written as [4]

$$\int Y Z d\mathbf{v} = -\frac{(q_x)_Y}{T^2} \frac{\partial T}{\partial x}. \quad (24)$$

Here $(q_x)_Y$ is the heat flux associated with the distribution function Y . This equation gives a physical meaning to condition (21). Varied distribution functions are selected in such a way that the entropy production due to the molecular collisions is equal to the entropy production due to the heat conduction. In other words entropy produced by molecular collisions is equal to the product of the heat flux and conjugated thermodynamic force. This condition is in accordance with the starting assumption of a stationary process.

The multiplication of the Boltzmann equation with the perturbative distribution function Ψ and integration over molecular velocity space \mathbf{v} gives

$$\int \Psi Z d\mathbf{v} = - \int \Psi \hat{O} \Psi d\mathbf{v}. \quad (25)$$

Using conditions (16-18) we get,

$$\int (\Psi - Y) \hat{O} (\Psi - Y) d\mathbf{v} \geq 0, \quad (26)$$

$$\int \Psi \hat{O} \Psi d\mathbf{v} + \int Y \hat{O} Y d\mathbf{v} - \int \Psi \hat{O} Y d\mathbf{v} - \int Y \hat{O} \Psi d\mathbf{v} = \int \Psi \hat{O} \Psi d\mathbf{v} + \int Y \hat{O} Y d\mathbf{v} - 2 \int Y \hat{O} \Psi d\mathbf{v} \geq 0, \quad (27)$$

$$\int \Psi \hat{O} \Psi d\mathbf{v} + \int Y \hat{O} Y d\mathbf{v} + 2 \int Y Z d\mathbf{v} = \int \Psi \hat{O} \Psi d\mathbf{v} + \int Y \hat{O} Y d\mathbf{v} - 2 \int Y \hat{O} Y d\mathbf{v} = \int \Psi \hat{O} \Psi d\mathbf{v} - \int Y \hat{O} Y d\mathbf{v} \geq 0, \quad (28)$$

$$\int \Psi \hat{O} \Psi d\mathbf{v} \geq \int Y \hat{O} Y d\mathbf{v}. \quad (29)$$

The left-hand side is the entropy production of the rarefied gas. It comes from Eq. (29) that solutions of the Boltzmann equation are in accordance with MEP principle.

There is another approach to this problem which has been proposed by Kohler [4]. Due to the fact that Eq. (24) is proportional to the heat flux he had fixed the heat flux and varied the distribution function under constraint

$$q_x = \text{constant}. \quad (30)$$

We note that due to the already fixed temperature field the entropy production is also fixed. Kohler did not impose stationary conditions on the trial distribution function. In his approach the entropy generated by molecular collisions need not be equal to the entropy produced by fluxes and gradients. If one does not take care of this inconsistency the conclusion can be reached, by using the calculus of variation, that solutions of the Boltzmann equation are those that generate minimum entropy production

V. CONCLUSION

The Onsager principle of the least dissipation of energy is valid for processes close to the equilibrium state. In this paper the equivalence between the Onsager principle of the least dissipation of energy and the MEP principle is established. Starting from the fact that fluxes are the main phenomenological characteristic of irreversible processes we have expanded the density of entropy production as the function of fluxes up to the second order. We have found that the dissipation function introduced by Onsager is the entropy production in the space of the fluxes. Invoking the first law of thermodynamics the equivalency between the Onsager principle of the least dissipation energy and the MEP principle is established.

It follows from the Boltzmann equation that entropy production is quantitatively related to the collision integral. Collisions between molecules in nonequilibrium state produce entropy. In this paper the solutions of the linearized Boltzmann equations are considered. It is found that these solutions correspond to the extremum of entropy production. The nature of the extremum depends on the constraints. Assuming that the entropy produced by molecular collisions is equal to the entropy productions due to the heat conductions or/and viscosity we find that the solutions of the Boltzmann equation satisfy the MEP principle.

The principle of minimum entropy production is valid if one grants fixed fluxes. However, the starting assumption of the fixed thermodynamic forces and the additional assumption of fixed fluxes leave no room for variation. Although both approaches are equivalent from the mathematical point of view one has to notice that the assumption of fixed fluxes is not consistent with the starting assumption of the stationary process. Namely, the additional request that entropy produced by molecular collisions need not be equal to the entropy production described by thermodynamic forces contradicts the starting assumption of the stationary process.

In short, revisiting the linear nonequilibrium thermodynamics and linearized Boltzmann equation shows that both approaches are in accordance with the MEP principle. Generally we can conclude that the MEP principle is valid for processes close to the equilibrium state.

Acknowledgements

The present work was supported by the bilateral research project of the Slovenia-Croatia Cooperation in Science and Technology, 2009-2010 and Croatian Ministry of Science grant No. 177-1770495-0476 to DJ.

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